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Assessing the drivers of dissolved organic matter export from two contrasting lowland catchments, U.K

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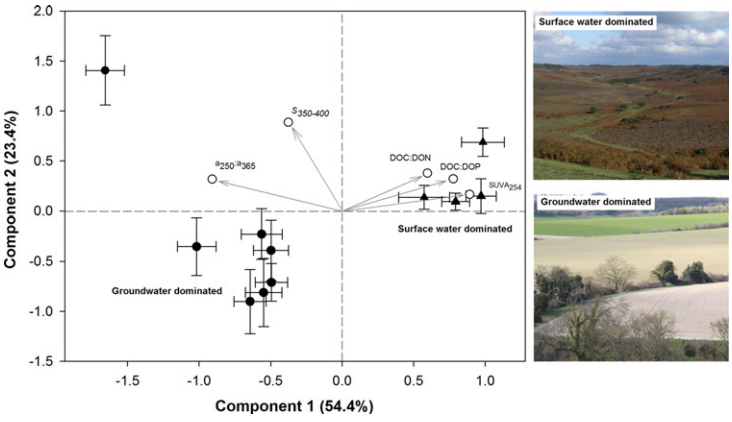
HIGHLIGHTS

- Controls on dissolved organic matter quantity and composition investigated in lowland catchments.
- Catchments differed in dominant flow pathways (groundwater vs. surface water dominated).
- Significant differences between organic matter composition observed between catchments.
- Hydrology and land cover identified as likely controls on organic matter composition.

GRAPHICAL ABSTRACT



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ABSTRACT

Two lowland catchments in the U.K. were sampled throughout 2010–11 to investigate the dominant controls on dissolved organic matter quantity and composition. The catchments had marked differences in terms of nutrient status, land cover and contrasting lithologies resulting in differences in the dominant flow pathways (groundwater vs. surface water dominated). The Upper Wylye is a chalk stream with a baseflow index of 0.98, draining a catchment dominated by intensive agricultural production. Millersford Brook is a lowland peat catchment with a baseflow index of 0.43, draining a semi-natural catchment with heather moorland and coniferous forest. Samples were collected weekly between October 2010 and September 2011 from eleven sampling locations. Samples were analysed to determine dissolved organic carbon, nitrogen and phosphorus fractions with DOM composition evaluated via the DOC:DON ratio, DOC:DOP ratio, specific UV absorption at 254 nm, absorbance ratio (a_{250}:a_{365}) and the spectral slope parameter between 350 and 400 nm ($S_{350–400}$). Significant differences were observed in all determinands between the catchments, over time, and spatially along nutrient enrichment and geoclimatic gradients. Seasonal variation in preferential flow pathways mobilising groundwater-derived DOM were identified as likely controls on the delivery of DOM in the permeable chalk dominated catchment. Steeper $S_{350–400}$ values and elevated a_{250}:a_{365} ratios in this catchment suggest material of a lower bulk aromatic C content and molecular weight delivered during the winter months when compared to the summer. DOC:DON ratios were markedly lower in the chalk catchment than the peatland catchment, reflecting the paucity of organic matter within the

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mineral soils of the chalk landscape, and higher fertiliser application rates. This manuscript highlights that DOM composition varies according to catchment landscape character and hydrological function.

1. Introduction

The pool of dissolved organic matter (DOM) in aquatic ecosystems is dynamic, consisting of a wide range of compounds with differing chemical structures and reactivities. As a result DOM has a multifaceted role in the biogeochemistry of aquatic ecosystems, impacting upon ecosystem production (Lindell et al., 1996), complexation of trace metals (Christensen et al., 1996; Brooks et al., 2007) and the mobilisation of pollutants (Aiken et al., 2011; Deb and Shukla, 2011). Additionally, in both freshwater and marine systems DOM acts as a major global carbon reservoir (Battin et al., 2008; Waeles et al., 2013) while also containing significant concentrations of organically bound nutrients such as dissolved organic nitrogen (DON) and phosphorus (DOP). These constituents have been found to be important, as low molecular weight (LMW) DOM (e.g. amino acids, polyamines, nucleotides) have been shown to be directly available for plant and algal uptake (Chapin et al., 1993; Lipson and Näsholm, 2001; Jones et al., 2005; Fransson and Jones, 2007; Jansson et al., 2012). Similarly, high MW (HMW) DOM is known to be available for microbial assimilation in terrestrial and aquatic environments (Antia et al., 1991; Seitzinger and Sanders, 1997), and to be susceptible to photodegradation, liberating bio-available inorganic or LMW organic C, N and P for microbial utilisation (e.g. Mostafa et al., 2007).

Organic nitrogen has been found to be an important form of nitrogen exported from the terrestrial environment to aquatic systems across a range of environments (Johnes and Burt, 1991; Prior and Johnes, 2002; Perakis and Hedin, 2002; Siemens and Kaupenjohann, 2002; Mattsson et al., 2005). A similar pattern is evident globally wherever intensive agriculture is practiced together with the expansion of population in urban and rural settlements (Vitousek et al., 2009; Durand et al., 2011). DOP has received less attention to date, but nevertheless comprises a significant proportion of the total P flux to freshwaters, particularly in intensively farmed and heavily populated catchments (e.g. Prior and Johnes, 2002) and in coastal and oceanic systems (e.g. Karl and Björkman, 2002; Ruttenberg and Dyhrman, 2012).

A comprehensive understanding of how the nutrient content of freshwater DOM varies relative to anthropogenic and geoclimatic controls is currently lacking. Historically, the majority of studies investigating DOM dynamics in freshwater catchments in the U.K. have focussed on upland and peat-dominated catchments due in part to rising trends in DOC export (Evans et al., 2006). This has led to a lack of understanding of both the composition and the processes dominating the delivery of organic material to lowland catchments where climate, geology and human alteration of the landscape are markedly different to the conditions in upland landscapes. Anthropogenic perturbation also has the potential to impact upon both the concentration and composition of DOM exported from these landscapes. Recent research by Graeber et al. (2015) observed shifts in DOM composition as a function of increasing agricultural land cover with decreasing C:N ratios and a more microbial DOM composition based on analysis of the chromophoric DOM (CDOM) fraction. It was also suggested that these compositional differences will likely result in enhanced reactivity of catchment DOM emissions fuelling biogeochemical processing in fluvial systems.

Lowland catchments in the U.K. tend to have intensively farmed landscapes, higher population densities and a high proportion of flow moving along throughflow and baseflow pathways linking source to stream. Baseflow indices usually vary between 0.5 in clay catchments to over 0.95 in catchments underlain by permeable bedrock such as chalk or Jurassic Limestone (Gustard et al., 1992). Permeable catchments are underlain by economically significant aquifers where abstraction for industrial, agricultural and domestic consumption alters the natural hydrological function of catchments. Such systems are hydrologically different from the more commonly studied upland peat catchments, and have moderate flow regimes, fewer peak flow events over the year and higher flow in the summer months where streamflow is supported by discharge from groundwater (Johnes, 2007). Delivery pathways and the flushing of landscape stores of DOM to streams are therefore likely to be different from upland and peatland catchments with a low baseflow index, where catchment hydrology is dominated by high flow events mobilising the flushing of catchment stores of very different chemical character. The composition of DOM flushed from these different stores along these differing pathways is then likely to vary, according to the specific character of the catchment, suggesting that knowledge acquired in upland or peatland catchments on DOM flushing behaviour and character may not be directly transferable to lowland and intensively farmed or populated catchments.

Recent studies have extensively utilized optical measurements of the CDOM fraction of DOM to provide useful insights into DOM composition at high temporal resolution, as characteristics of the optically active DOM pool can be related to its source and biogeochemical role (Fellman et al., 2010; Spencer et al., 2012). CDOM absorbs light in the visible, UV-A and UV-B wavelength ranges. Parameters derived from CDOM absorption spectra have been used to distinguish compositional characteristics of DOM enabling greater insights to be gained when investigating source and degradation state across a range of environments (Helms et al., 2008; Spencer et al., 2007; Peter et al., 2012). These commonly utilized parameters include DOC concentration normalised to UV absorbance at 254 nm ($SUVA_{254}$), absorbance ratios such as a_{250}:a_{365} along with examination of the spectral slope parameter (S) over a number of wavelength ranges (Weishaar et al., 2003; De Haan and De Boer, 1987; Helms et al., 2008).

This paper presents the outcomes from a research programme undertaken to determine the relative importance of DOM as a component of C, N and P pools from land to stream in lowland catchments, while also assessing the composition of DOM in each system as this varies in relation to the land cover and hydrological function of each catchment over the annual cycle. It is hypothesised that DOM composition will vary between catchments as a function of geoclimatic character and nutrient enrichment status, with hydrological function being a key control in temporal variation in DOM composition.

2. Materials and methods

2.1. Study area

In order to assess the impact of landscape character and hydrology on the relative contribution of DOM to nutrient transfer and the composition of this flux, two lowland catchments of contrasting character were selected for this study. Both are sub-catchments of the Hampshire Avon, U.K., with comparable altitude and climate, removing these as variables in this study. Each has marked longitudinal gradients in both nutrient enrichment status and landscape character from their headwaters to their lowest reaches.

The Wylye catchment (Fig. 1) lies to the west of the main River Avon, rising south of Maiden Bradley, flowing north-east through the villages of Kingston Deverill, Brixton Deverill and Longbridge Deverill, and then north to the town of Warminster before turning south-east towards the city of Salisbury. It has its confluence with the Avon at Wilton, north of Salisbury. This research programme focused on the Upper Wylye,

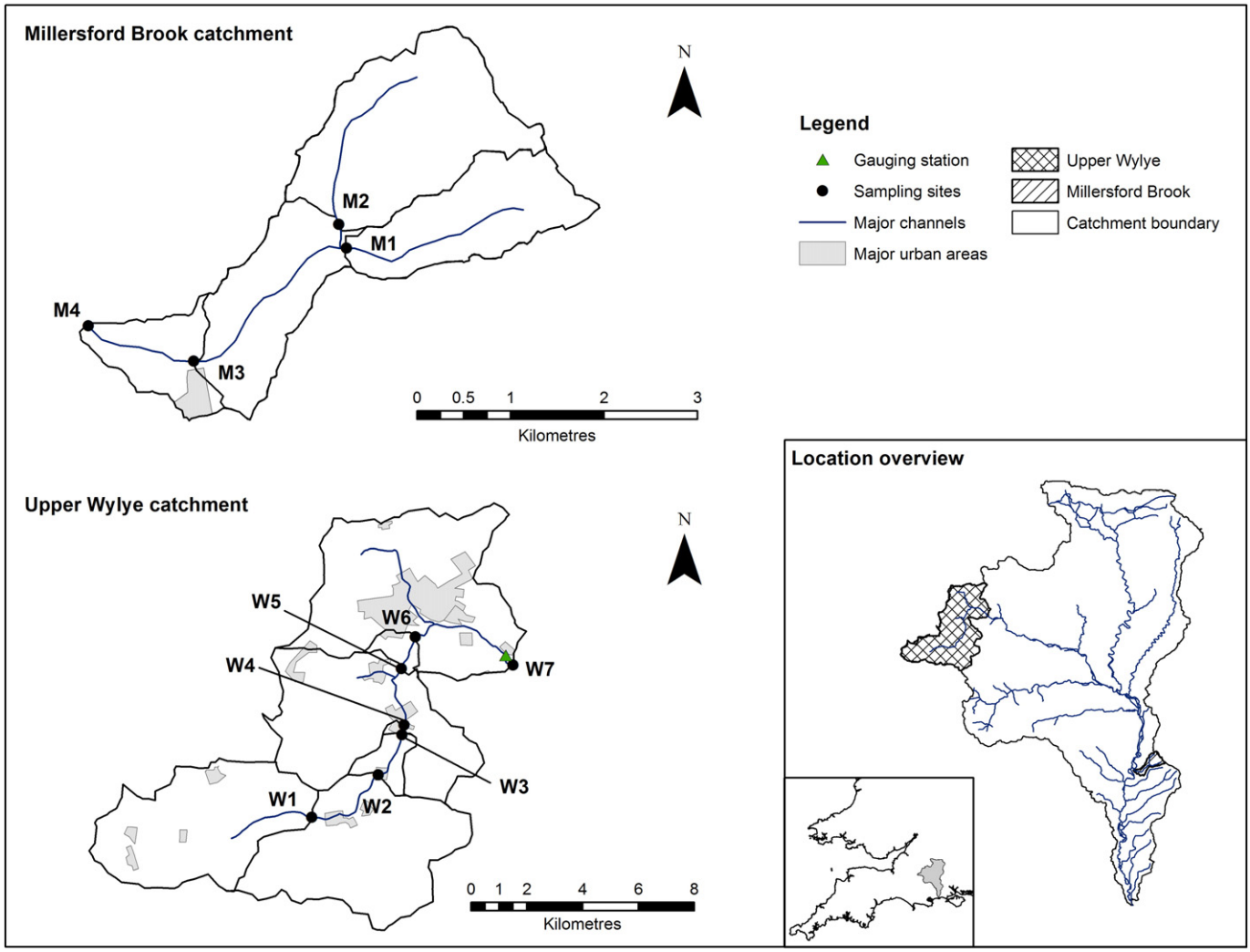

Fig. 1. Upper Wylye and Millersford Brook study locations including catchment reach structure. M1–4 = Millersford Brook, W1–7 = Upper Wylye.

upstream from the Environment Agency gauging station at Norton Bavant (Station ID: 43012), which has a catchment area of 116 km^2. Its geology is predominantly chalk, a porous, calcareous sedimentary rock, with some Upper Greensand comprising fine-grained glauconitic sands and sandstones which locally reduce permeability (Allen et al., 2014). The chalk provides a significant groundwater aquifer and a major source of domestic water supply in the region. Its altitude varies from its highest point of 245 m OD at White Sheet Down on its western catchment boundary to 105 m OD at the study catchment outlet at Norton Bavant, and receives an average annual rainfall of 921 mm (SAAR6190: National River Flow Archive).

The upper reaches of the Wylye are ephemeral, and the perennial head is located at Kingston Deverill (Fig. 1). Mean daily discharge in the Wylye at Norton Bavant was 0.695 m^3 s^{-1} (184 mm yr^{-1}) over 2011–12 with maximum flows occurring in January–February and minimum flows from September to October, with the seasonal hydrograph strongly influenced by a complex abstraction and stream support regime operated by the local water company. Wessex Water operates a public water supply abstraction borehole at Brixton Deverill, with up to 18 ml/day abstracted for public supply. Much of the water is exported out of the catchment to supply nearby urban centres at Bath, Trowbridge and Yeovil. To mitigate the environmental impact of abstraction, stream support is provided with up to 10 ml/day pumped into the river at Kingston Deverill and 8.64 ml/day at Brixton Deverill to maintain minimum prescribed flows. In the period of study, stream support accounted for an average of 52% of total annual flow at Brixton Deverill, though its relative importance varied seasonally: stream support was largely absent between February and May due to increased frequency of rainfall. The impact of augmentation is reduced downstream at Norton Bavant as minor unsupported tributaries contribute to total flow along with augmentation from effluent discharges from the groundwater aquifer. Stream support accounted for approximately 24% of total instream flow in 2011 at Norton Bavant.

The soils of the Upper Wylye are predominantly calcareous brown earths: non-alluvial loam or clay soils with a weathered calcareous subsoil, low organic content and a high infiltration capacity. These are underlain by porous chalk bedrock, promoting throughflow and groundwater discharge as the dominant flow pathways throughout the catchment. The baseflow index (0.98) reflects the dominance of these subsurface flow pathways in the annual hydrograph of the Upper Wylye. Natural organic matter sources in the catchment are limited. Land use in the catchment is dominated by arable agriculture (44.7%) with calcareous grassland (8.67%), broadleaf woodland (6.79%) and coniferous woodland (4.91) also present. A summary of land use classifications can be found in Table 1. The majority of dwellings in the upper catchment are located in riparian villages and are not connected to mains sewerage. Septic tank systems are commonplace and the Wylye receives discharge from 158 septic tanks under effluent discharge licences granted by the Environment Agency to individual dwellings upstream from Warminster. At Warminster there

Table 1
Land use classification summary for delineated catchment reaches.

Land classification	Millersford Brook catchment				Upper Wylye catchment						
	M1 (%)	M2 (%)	M3 (%)	M4 (%)	W1 (%)	W2 (%)	W3 (%)	W4 (%)	W5 (%)	W6 (%)	W7 (%)
Improved grassland	–	7.9	12.3	16.6	28.6	25.3	24.9	25.0	27.5	27.9	27.0
Dwarf shrub heath	86.9	62.1	60.4	54.2	–	–	–	–	–	–	0.003
Rough low-productivity grassland	1.08	1.81	4.73	5.41	3.23	3.77	3.75	3.73	3.54	3.55	3.33
Broad leaved, mixed woodland	5.87	14.6	11.9	12.8	2.95	0.15	2.82	2.83	5.21	5.19	6.79
Arable and horticulture	–	2.0	2.26	2.84	55.6	59.0	57.9	57.8	51.2	50.9	44.7
Coniferous woodland	6.12	7.99	5.70	5.34	0.10	0.15	0.14	0.13	4.43	4.28	4.91
Neutral grassland	0.004	–	0.16	0.14	–	–	–	–	–	–	–
Built up areas and gardens	–	3.18	2.32	2.52	0.24	0.29	0.26	0.27	0.46	0.51	4.28
Fen marsh and swamp	–	0.47	0.25	0.23	–	–	–	–	–	–	0.01
Calcareous grassland	–	–	–	–	9.21	11.1	10.2	10.2	7.39	7.29	8.67
Freshwater	–	–	–	–	–	0.09	0.09	0.08	0.28	0.28	0.22
Inland rock	–	–	–	–	–	–		–	–	0.17	0.12
Acid grassland	–	–	–	–	–	–		–	0.01	0.03	0.02
Total area (km^2)	2.43	3.93	7.29	8.13	26.5	52.7	55.8	56.1	81.2	82.4	116

is a major point source input in the form of treated effluent discharged from Warminster Wastewater Treatment Works (WwTW) which, since 2001 has been subject to P stripping under the 1991 EU Urban Wastewaters Treatment Directive (UWwTD, 91/271/EEC).

The Millersford Brook catchment (Fig. 1) receives a similar average annual rainfall to the Upper Wylye at 854 mm (SAAR6190: National River Flow Archive), with altitude ranging from 125 m on its eastern catchment boundary to 40 m at the study catchment outlet at Folds Farm, but has markedly different landscape characteristics. It is a semi-natural moorland catchment located in the south east of the Hampshire Avon catchment. Land use (Table 1) is dominated by dwarf shrub heath (54%) mainly in the north of the catchment with its southern reaches dominated by improved (16.6%) and low productivity grassland (5.41%). It is the most northerly of the small streams in the western New Forest plateau, draining south west from its moorland headwaters at site M1, receiving agricultural runoff from several small, low stocking density horse grazing fields at site M2 (Millers Ford) before passing through the small settlement north of Godshill (site M3) and through Folds Farm (site M4) before joining the main channel of the River Avon north of Fordingbridge. It has a catchment area of 8.13 km^2, and its geology is dominated by glacial clay, sandstone and river gravels overlain by thin peat soils, with valley bottom mires as a typical feature of the catchment. Drainage is impeded by valley aquitards, and the baseflow index is 0.34, with a much higher proportion of flow from land to stream delivered via surface than groundwater flow pathways in comparison to the Upper Wylye catchment.

Mean daily discharge rates in the lower reaches of Millersford Brook were significantly lower than in the upper reaches of the Wylye at $<0.1\ m^3\ s^{-1}$ reflecting the smaller stream channel and catchment size at Millersford Brook. However, at 378 mm yr^{-1} over 2011–12 it had double the rate of runoff compared to the Upper Wylye (184 mm yr^{-1}), reflecting the differences between this surface flow dominated catchment and the groundwater dominated Wylye catchment. Maximum flows in Millersford Brook coincided with periods of intense rainfall between November to March and minimum flows from April to July.

2.2. Sample collection, preservation and storage

Water samples were collected weekly along the Upper Wylye (seven sites) and at one tributary stream and three sites along the Millersford Brook. Samples were collected on the same sampling day at all sites, across a wide range of hydrometeorological conditions between October 2010 and September 2011 (Fig. 2). On arrival at the laboratory an unfiltered aliquot was decanted for subsequent total N and total P analysis, and a second aliquot was immediately vacuum filtered through a pre-leached 0.45 μm cellulose nitrate filter for inorganic N and P analysis. All samples for DOC analysis and CDOM optical characterisation were separately filtered through 0.7 μm pre-combusted (450 °C) glass-fibre filters (Whatman GF/F). All samples were stored in the dark at 4 °C to inhibit microbial degradation with analyses conducted within 24 h of sample collection.

2.3. Analytical methods

2.3.1. Determination of N species and P fraction concentrations

Inorganic nutrient analyses were conducted on filtered samples using a Skalar San^{++} multi-channel continuous flow autoanalyser with channels set up for simultaneous determination of total oxidised nitrogen (nitrate as NO_3-N, plus nitrite as NO_2-N) hereafter referred to as TON, total ammonium (NH_3-N + NH_4-N) and soluble reactive phosphorus (SRP, measured as PO_4-P) analyses. TON analyses were based on the hydrazine-copper reduction method producing a reddish-purple azo dye measured colourimetrically at 540 nm. Total ammonium was determined by use of a modified Berthelot reaction, producing a green complex measured colourimetrically at 660 nm. SRP was also determined colourimetrically following reaction with heptamolybdate and potassium antimony (III) oxide tartrate in acidic solution followed by reduction with ascorbic acid, measured colourimetrically at 880 nm.

Total Dissolved Phosphorus (TDP) and Total Dissolved Nitrogen (TDN), determined on filtered samples, and Total Phosphorus (TP) and Total Nitrogen (TN), determined on unfiltered samples, were determined simultaneously using the persulphate oxidation method of Johnes and Heathwaite (1992) modified for the CEM Mars Xpress microwave digestion unit (Yates and Johnes, 2013). Sample digests were then analysed colourimetrically using the Skalar San^{++} autoanalyser methods for TON and SRP. Dissolved Organic Phosphorus (DOP) was calculated as the difference between TDP and SRP concentrations, with Dissolved Organic Nitrogen (DON) calculated as the difference between total inorganic N fraction concentrations (TON plus total ammonium) and TDN. Particulate Phosphorus (PP) and Particulate Organic Nitrogen (PON) were calculated as the TN minus TDN and TP minus TDP respectively. QA checks were used to ensure the generation of robust data so that errors in calculated concentrations were minimised.

2.3.2. Determination of DOC and CDOM

DOC concentrations were measured as non-purgeable organic carbon on acidified samples (pH 2) determined by coupled high temperature catalytic oxidation using a Shimadzu TOC-L series analyser. The mean of three to five injections of 100 μl is reported for every sample. Measurement precision, described by the coefficient of variance (C.V) was <2% for the replicate injections.

Absorbance data were obtained using a Varian Cary 300 UV–Visible spectrophotometer on un acidified aliquots. Short pathlength cuvettes (10 mm) were used for all samples with an absorbance value of ≥0.02 at 350 nm. Samples where absorbance was <0.02 were analysed on a

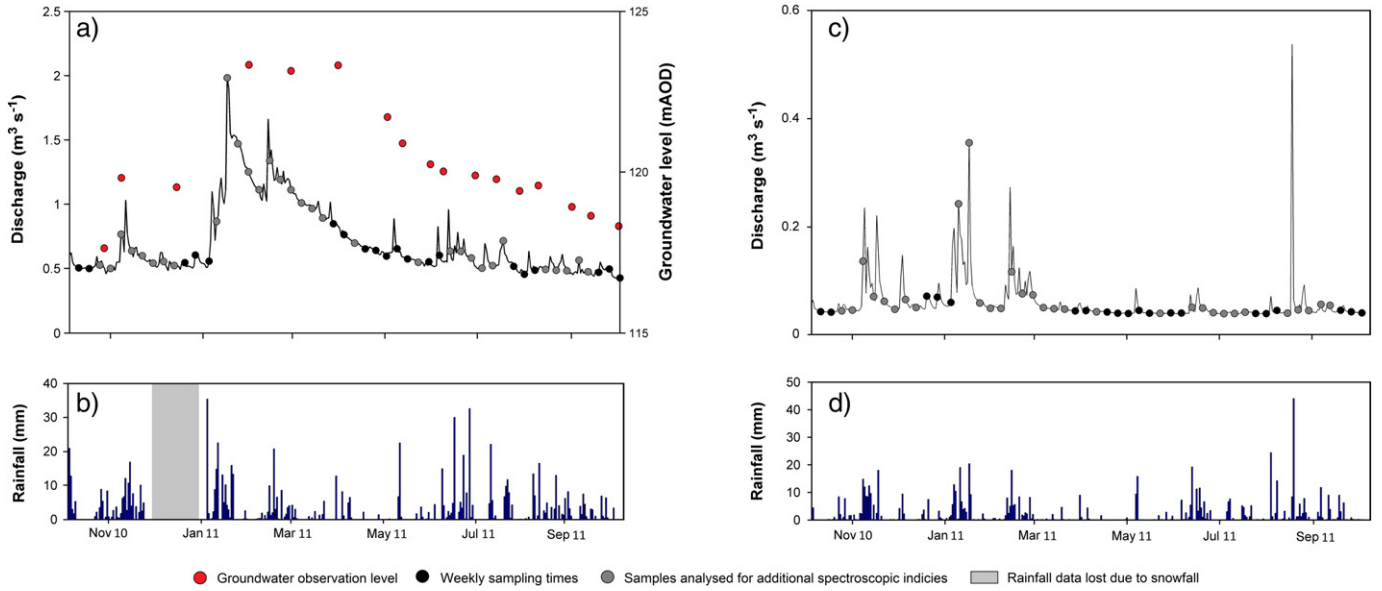

Fig. 2. Temporal variation in study catchment rainfall and river discharge; (a) Upper Wylye - mean daily discharge at Norton Bavant; (b) Upper Wylye - mean daily rainfall (station ID: 25001); (c) Millersford Brook - mean daily discharge at Godshill Wood; (d) Millersford Brook - mean daily rainfall (station ID: 30251). Weekly sampling dates are indicated by black circles; grey circles indicate samples analysed for additional spectroscopic analysis. Missing rainfall data due to snowfall indicated by grey area. Red circles indicate groundwater observation level data (Environment Agency).

longer pathlength cuvette (100 mm) with an integration time of 0.1 s. Absorbance spectra were scanned over the wavelength range 200–800 nm at 1 nm intervals. To minimise the effect of temperature on absorbance spectra, samples were allowed to reach a constant temperature (20 °C) prior to analysis. Minor corrections were made to account for entrapment of any glass fibres during filtration by subtracting the average sample absorbance between 750 and 800 nm. $SUVA_{254}$ values were calculated by dividing UV absorbance at 254 nm by DOC concentration (mg l^{-1}) (Weishaar et al., 2003). All absorbance data presented in this manuscript are expressed as absorption coefficients, as calculated below.

$$a(\lambda) = 2.303A(\lambda)/l$$

Where a(λ) is the absorption coefficient in units of reciprocal length (m^{-1}), A(λ) is raw absorbance and l is the cuvette pathlength (m). The factor of 2.303 allows conversion of logarithm base 10 to the natural logarithm. Spectral slope (S) values were calculated using a non-linear fit of an exponential function to the absorption spectrum over the range 350–400 nm (Helms et al., 2008).

$$a_{\lambda} = a_{\lambda\ ref}\ e^{-S(\lambda-\lambda_{ref})}$$

Where a, is the absorption coefficient, λ = wavelength (nm) and λ_{ref} is a reference wavelength (nm). $S_{275-295}$ data were also calculated however the data were not included in the analysis as it showed little spatial and temporal variation.

2.3.3. Calculating nutrient loading and molar ratios

Nutrient loading was calculated for C, N and P data using weekly paired instantaneous discharge and nutrient concentration data for each site (Johnes, 2007). Molar concentrations for each of the DOC, DON and DOP fractions were calculated for each sampling occasion. Molar DOC:DON and DOC:DOP ratios were calculated as an indicator of the relative composition of DOM instream (O'Donnell et al., 2012).

2.3.4. Statistical analysis

Catchment reach structures and land use were determined using ArcGIS (Esri) Hydrology toolbox based upon digital elevation models and land cover mapping (LCM2007) provided by the Centre for Ecology and Hydrology (U.K.). Flow data were obtained from the National Flow River Archive. Principle Component Analysis (PCA), a data transformation technique was used on all data collected (n = 143) for DOM quality indicators (DOC:DON, DOC:DOP, $SUVA_{254}$, a_{250}:a_{365} and $S_{350-400}$) to explore the underlying relationships in the dataset. One way ANOVA combined with Fisher's least significant difference test was used *post hoc* to investigate variation between sampling locations for all chemical determinands. Data that violated test assumptions (those that were not normally distributed) were log transformed where appropriate or the non-parametric equivalent Kruskal-Wallis one-way ANOVA test was applied. All analyses were conducted using SPSS® Statistical software, version 23 (IBM®).

3. Results

3.1. Inter-basin comparison of C, N and P flux in the headwaters of each catchment

Headwater sampling locations in both study catchments can be considered endmember sampling locations reflecting the key contributing source areas at the head of each stream. Land use in the headwaters of the Upper Wylye catchment are dominated by arable cultivation (55.6%) and improved grassland (28.6%), while the headwater reach of Millersford Brook is dominated by dwarf shrub heathland typical of moorland vegetation in the U.K. (86.9%) with minor areas of coniferous woodland (6.12%) and broad leaved, mixed woodland (5.87%). There is no agricultural land in the Millersford Brook catchment above the headwater sampling site at M1. As a result inorganic nutrient fractions differ significantly with both mean TON and SRP concentrations elevated in the upper reaches of the Wylye (7.11 mg l^{-1} and 95 μg l^{-1} respectively; Table 1, Supplementary information) reflecting the agricultural nature of the catchment. By contrast, the upper reaches of Millersford Brook at site M1 recorded a mean TON concentration of 0.132 mg l^{-1} and

mean SRP concentration of 8 μg l^{-1} (Table 1, Supplementary information) over the period of study, reflecting the conservative cycling of inorganic nutrient fractions in moorland ecosystems where nutrient enrichment from anthropogenic activities are typically lacking. Organically bound nitrogen and phosphorus fractions also differ in their relative contribution to total N and total P concentrations recorded in the two catchments. DON and DOP concentrations are similar in both catchments at 0.766 mg N l^{-1} and 29 μg P l^{-1} at site W1, and 0.547 mg N l^{-1} and 33 μg P l^{-1} at site M1 (Table 1, Supplementary information). As a result, while DON accounts for an average 8% of TN in the headwaters of the Wylye, it accounts for 66% of TN in the upper reaches of Millersford Brook. Similarly, DOP accounts for 16% of TP at site W1 compared to 71% of TP at site M1. DOC concentrations in the Wylye at site W1 ranged from 0.77 to 4.16 mg C l^{-1} (mean, 1.52 mg C l^{-1}) and concentrations in Millersford Brook at site M1 range from 3.88 to 14.5 mg C l^{-1} (mean, 8.56 mg C l^{-1}; Table 1, Supplementary information). Concentration ranges of DOC across both catchments reflect their underlying geologies and soil types, with waters draining the peat soils of the Millersford Brook catchment having substantially higher DOC concentrations compared to waters draining through the chalk matrix and from the calcareous brown earth soils of the Upper Wylye catchment.

Annual nutrient loading calculated for each catchment is presented in Table 2, Supplementary information. This demonstrates further the differences in inorganic and organic nutrient delivery between these systems with 8.51 kg ha^{-1} a^{-1} TON and 0.681 kg ha^{-1} a^{-1} DON delivered to the Wylye at W1 compared to 0.38 kg ha^{-1} a^{-1} TON and 1.65 kg ha^{-1} a^{-1} DON in Millersford Brook at M1. A similar difference in loading is observed in SRP between the two sites, with the delivery of 0.105 kg ha^{-1} a^{-1} SRP in the Upper Wylye at site W1, compared to 0.021 kg ha^{-1} a^{-1} SRP in the headwaters of Millersford Brook, though total P loading is comparable in both sites at 0.133 kg ha^{-1} a^{-1} TP in the Wylye at W1, and 0.130 kg ha^{-1} a^{-1} in Millersford Brook at M1. As with the loading data for nitrogen, DOP contributes a higher proportion of the TP load in the peatland catchment (0.089 kg ha^{-1} a^{-1}, 68.5% of TP load) than in the chalk catchment (0.021 kg ha^{-1} a^{-1}, 15.8% of TP load). These differences in loading reflect the dominant land use classes in the upper reaches of the catchment and the intensity of agricultural production in the upper reaches of the Wylye compared to Millersford Brook. The difference in DOC loading is also marked, with Millersford Brook transporting a total load of 26.6 kg ha^{-1} a^{-1} DOC, compared to 2.32 kg ha^{-1} a^{-1} in the Upper Wylye, reflecting the carbon-rich soils in the peatland catchment, compared to the mineral soils of the chalk catchment.

3.2. Spatial and temporal variation of C, N and P

Mean annual nutrient concentration data, spectroscopic CDOM indices and molar DOC:DON and DOC:DOP for the Upper Wylye and Millersford Brook sampling sites are presented in Table 1,

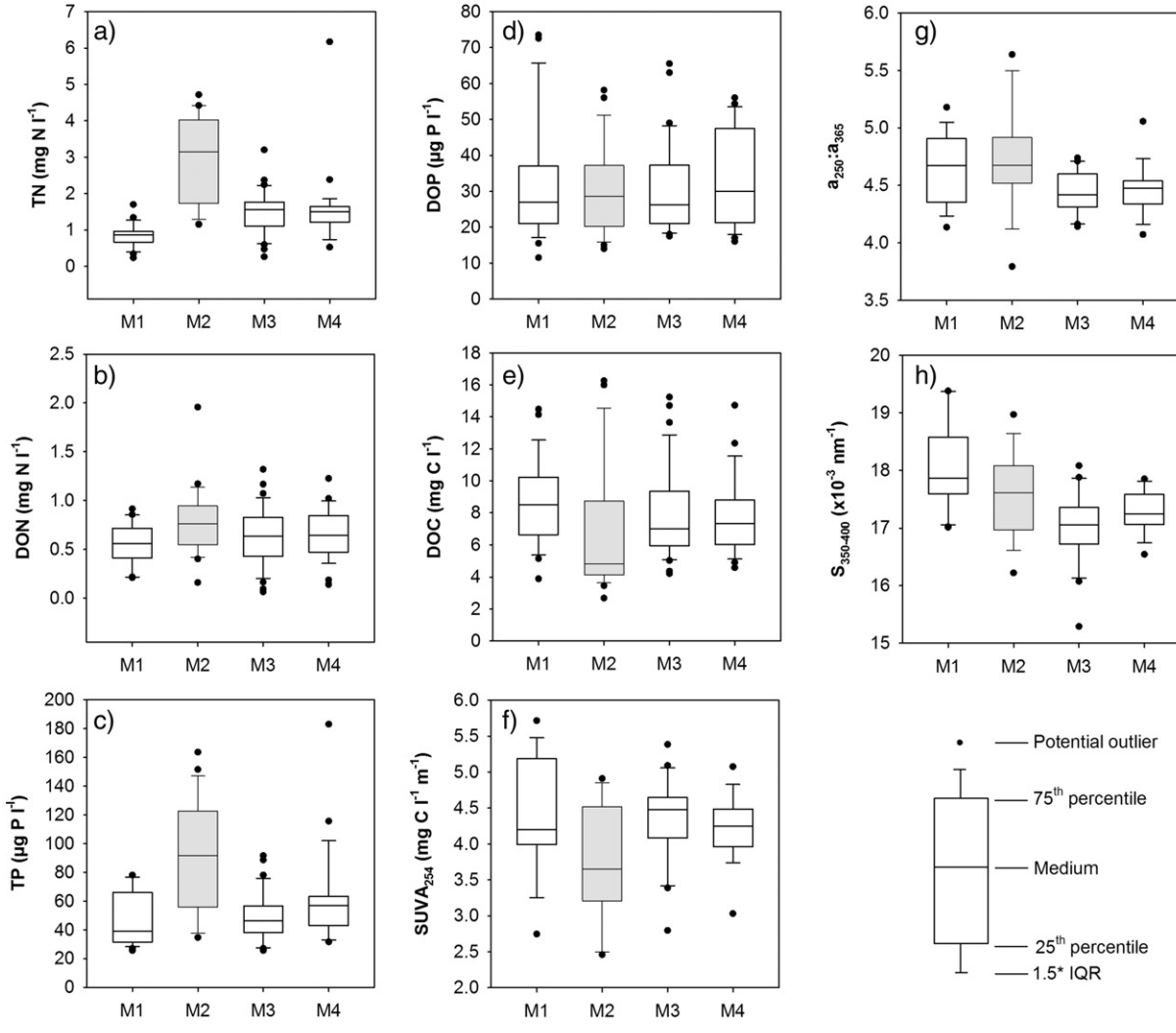

Fig. 3. Statistical boxplots representing longitudinal trends in nutrient chemistry and spectroscopic indices in the Millersford Brook catchment. Samples representing minor tributaries are shown in grey. Boxes represent interquartile range (IQR) and whiskers encompass 1.5 IQR.

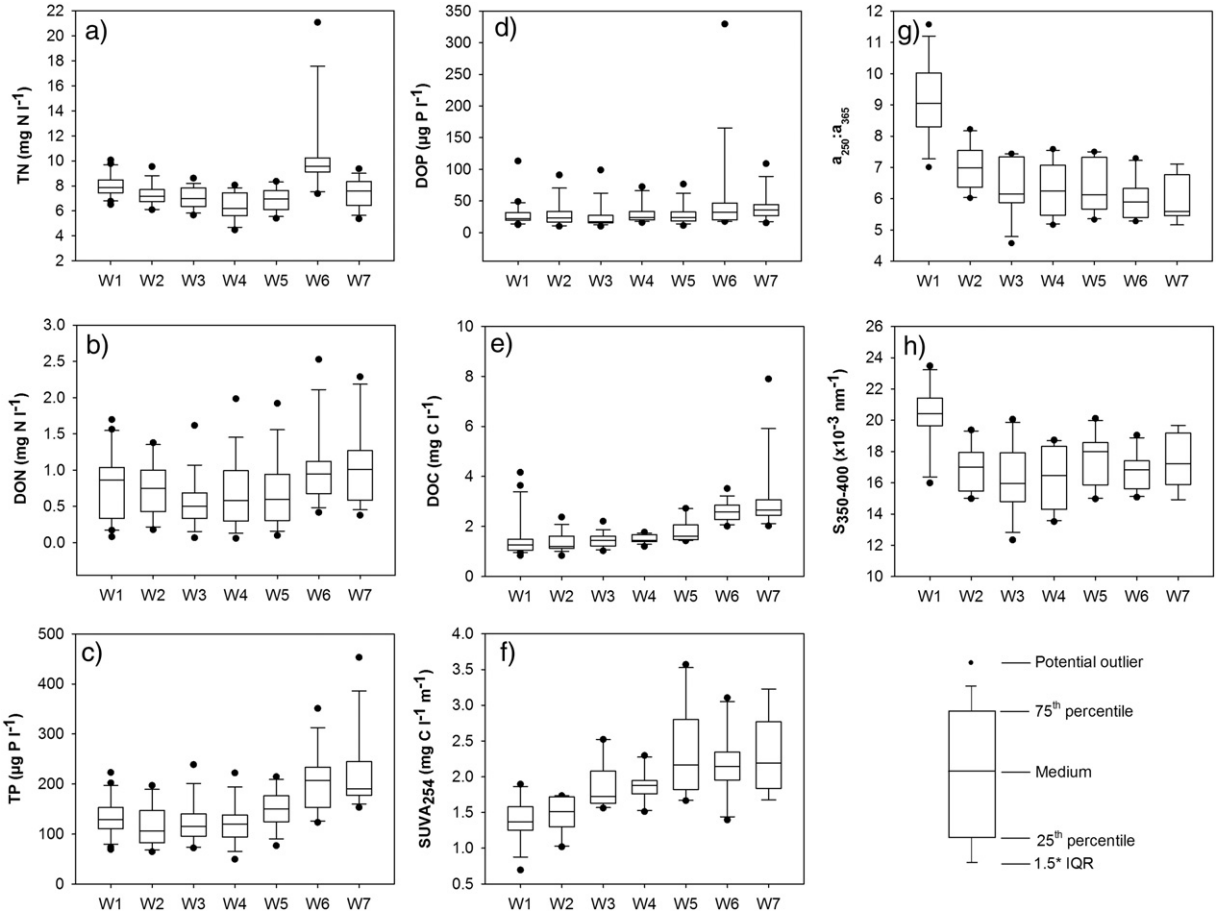

Fig. 4. Statistical boxplots representing longitudinal trends in nutrient chemistry and spectroscopic indices in the Upper Wylye catchment. Boxes represent interquartile range (IQR) and whiskers encompass 1.5 IQR.

Supplementary information, while Figs. 3 and 4 present longitudinal trends in these chemical and optical parameters for Millersford Brook and the Upper Wylye respectively.

In Millersford Brook, longitudinal trends are evident in each of these metrics. Significant differences in TON and SRP concentrations ($p < 0.05$) were found between headwater site M1 and the sampling location on the tributary stream at M2 with TON increasing from M1 = 0.132 mg N l^{-1} to M2 = 2.43 mg N l^{-1}, and SRP increasing from M1 = 8 µg P l^{-1}, M2 = 24 µg P l^{-1}. While no differences were observed in DOP concentrations between these sites, DON showed a similarly significant ($p < 0.05$) increase in concentration from site M1 (0.547 ± 0.202 mg N l^{-1}) to M2 (0.775 ± 0.351 mg N l^{-1}). Shifts were also observed in the dominance of inorganic vs. organic nutrient fractions with organic N accounting for 66% of TN at the site M1 and only 31% at site M2. Similarly DOP accounts for 71% of TP at M1 and only 39% at M2, with the increase in TP concentration between the two sites contributed by increases in both SRP (an increase of 16 P µg l^{-1}) and particulate P (an increase of 34 µg P l^{-1}) over the period of study. Concentrations of DOC demonstrate a decrease between the two headwater sampling locations (M1 = 8.56 ± 2.61 mg C l^{-1}, M2 mean = 6.76 ± 3.96 mg C l^{-1}). These data suggest a shift in contributing source area to a less terrestrial organic matter rich origin draining M2 and is supported by land use data showing contrasts between the two headwater sites (Table 1). While improved grassland and built up areas and gardens comprise 7.9% and 3.18% of the total cover draining into site M2 these land use classes are absent from sub-catchment reach M1. Following the mixing of these two waters little longitudinal variation is observed between sites M3 and M4 with only significant increases in SRP concentrations observed (M3 = 12 ± 7 µg P l^{-1}, M4 = 22 ± 20 µg P l^{-1}). These longitudinal trends are reflected in the stoichiometric ratios in the DOM fraction for this catchment. The DOC:DON ratio varies from 21.4 ± 11.9 at site M1 in the headwaters of the stream, dropping to 17.1 ± 12 at site M4 at Folds Farm, with a lower value of 11.8 ± 7.5 in the tributary at M2 reflecting the higher proportion of improved and fertilised pasture in this catchment. The DOC:DOP ratio also drops along the length of Millersford Brook from 900 ± 568 at M1, to 691 ± 337 at M4, with the lowest ratio of 674 ± 532 in the tributary at M2.

By contrast, the landscape of the Upper Wylye is complex and as discussed by Yates and Johnes (2013) spatial variation in nutrient loading reflects the surrounding land use inputs (Fig. 4). DOC concentrations increase with distance downstream ranging from a mean concentration of 1.52 ± 0.86 mg C l^{-1} in the headwaters at site W1 to 1.81 ± 0.46 mg C l^{-1} at site W5. Following discharge from Warminster WwTW there is a significant increase in DOC concentration to a mean of 2.59 ± 0.39 mg C l^{-1}, increasing to 3.10 ± 1.46 mg C l^{-1} at Norton Bavant (W7) situated downstream from a further sewage discharge from a military barracks. A similar trend can be seen in DON data with a significant increase observed between sites W5 and W6 (W5 mean = 0.678 ± 0.473 mg N l^{-1}, W6 mean = 1.02 ± 0.550 mg N l^{-1}), with concentrations remaining constant between W6 and W7 (W7 mean = 1.06 ± 0.558 mg N l^{-1}). No significant increases in DOP concentrations were observed between these two sampling locations, though SRP concentrations rose from 95 ± 28 µg P l^{-1} at W6 to 144 ± 30 µg P l^{-1} at W7, suggesting increased delivery of these fractions from the military treatment works to the river. These longitudinal trends in the N speciation, P fractionation and DOC fluxes observed in the Upper Wylye are reflected in the stoichiometric ratios (Table 1,

Supplementary information). The DOC:DON and DOC:DOP ratio drops were 4.49 ± 5.83 and 177 ± 132 respectively at the groundwater-fed station at W1 and so very low. Moving downstream the DOC:DON ratios remained low and were further impacted by addition of DON relative to DOC by the WwTW effluent discharge at Warminster. By contrast, the DOC:DOP ratios rise at W6 and W7, reflecting the relatively high P content of this discharge, despite the implementation of P stripping processes at the works under the UWwTD since 1991.

These trends in the C:N:P ratio in the DOM fraction are also mirrored in the $SUVA_{254}$ and a_{254} data for the Upper Wylye. $SUVA_{254}$ values for riverine material often range between 1.8 and 4.8 mg C l^{-1} m^{-1} with higher values suggesting material derived from sources that are more aromatic such as vascular plant material (Creed et al., 2015). Calculated $SUVA_{254}$ values in the Upper Wylye range between 1.46 and 2.32 mg C l^{-1} m^{-1} across the Upper Wylye catchment suggesting a relatively lower aromatic C content in comparison to Millersford Brook. As $SUVA_{254}$ values increase with distance downstream in the Upper Wylye, both $S_{350–400}$ and a_{250}:a_{365} decrease.

Temporal variation in DOM quality, as reflected in the optical indices included in this study, is minimal in Millersford Brook (Fig. 5 a, b). During the winter months (December to February) $S_{350–400}$ ranged from 15.3 to 19.4 × 10^{-3} nm^{-1} with a mean of 17.7 × 10^{-3} nm^{-1}. Summer values (June to August) ranged from 16.2 to 19.3 × 10^{-3} nm^{-1} with a mean of 17.3 × 10^{-3} nm^{-1}. This is mirrored in the absorbance ratio, a_{250}:a_{365}, with winter mean values ranging from 4.3 to 5.2 (mean of 4.6), while summer values ranged from 4.1 to 6.6 (mean of 4.6). By contrast, over the 2011 hydrological year the Upper Wylye can be split into two periods with regards its optical properties (Fig. 5 c, d). Mean $S_{350–400}$ values during winter months were 18.6 × 10^{-3} nm^{-1} compared to a lower summer mean of 16.1 × 10^{-3} nm^{-1}. Similarly, mean a_{250}:a_{365} was higher during the winter months (7.2) compared to the summer mean of 6.4. Temporal patterns in $SUVA_{254}$, a common proxy indicator of percent aromaticity, are more difficult to distinguish, with little seasonal variation evident in these data sets. $SUVA_{254}$ values range between 0.9 and 3.2 mg C l^{-1} m^{-1} during the summer months with winter month $SUVA_{254}$ values ranging between 0.7 and 3.3 mg C l^{-1} m^{-1}.

Principle component analysis (PCA) was employed in order to separate sites by the maximum variation in DOM compositional measurements. The PCA identified 2 components with eigenvalues >1 explaining 77.8% of the variance in the data. DOC:DON, DOC:DOP and $SUVA_{254}$ correlated significantly with the positive axis of component 1 with a_{250}:a_{365} correlating negatively with component 1 explaining 54.6% of the total variance. $S_{350–400}$ correlated with the positive axis of component 2 explaining a further 23.4% of the total variance (Fig. 6). Cluster centroids representing the average score for each component with standard error (Fig. 6) are shown grouped into sites. Sites within Millersford Brook form a distinct cluster characterised by elevated DOC:DON, DOC:DOP and $SUVA_{254}$ values. Samples collected from the Upper Wylye catchment cluster in the negative axis of component 1 with lower DOC:DON, DOC:DOP and $SUVA_{254}$ values. Only site W1 plotted outside these clusters. This is a site receiving pumped groundwater recharge on a regular basis throughout the sampling period, with the chemistry more closely reflecting that of groundwater in this catchment.

Lastly, given the differences in DOM composition a linear regression was performed to examine the use of a_{254} to predict DOC concentrations across both catchments. Results demonstrated a strong positive relationship for all samples collected from Millersford Brook (Fig. 7a, r^2 = 0.88, $p < 0.001$) supporting numerous studies conducted in organic rich catchments dominated by soil and vascular plant material (Spencer et al., 2012; Avagyan et al., 2014). However, data observed from the Upper Wylye where DOC concentrations are significantly lower, demonstrate a more complex relationship. While a linear

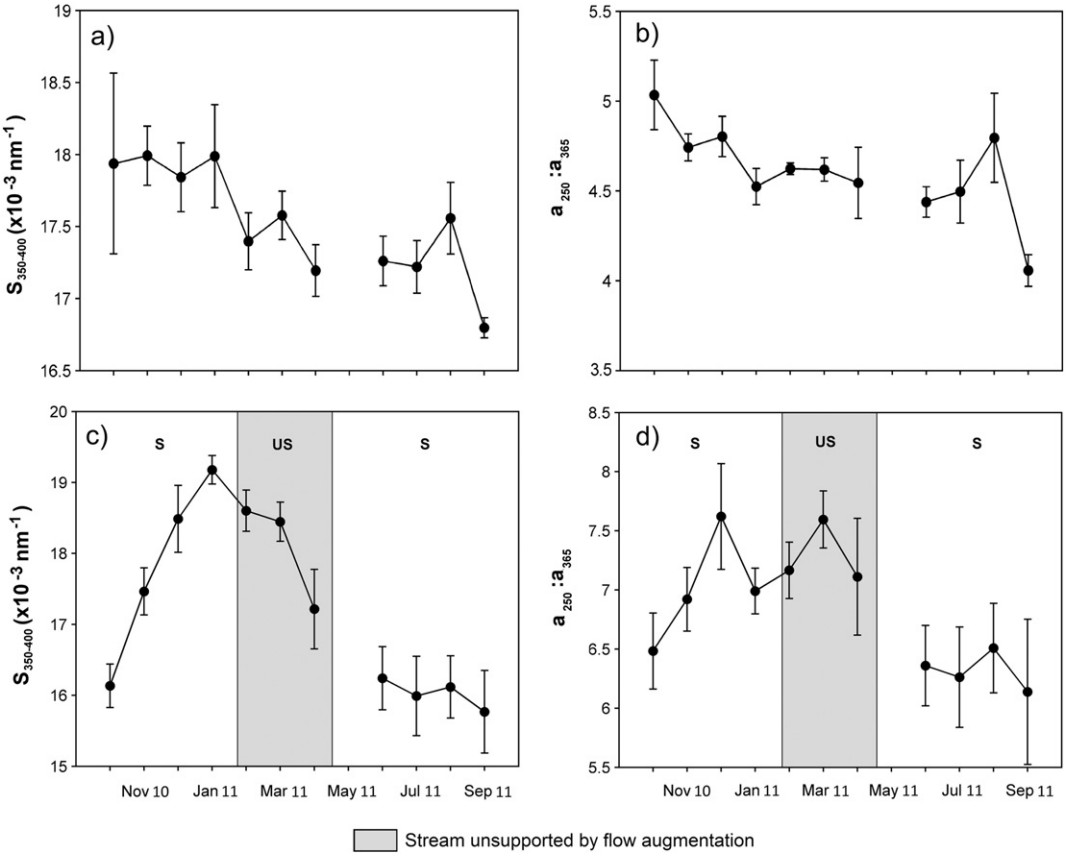

Fig. 5. Time series of selected spectroscopic indices collected across the Millersford Brook (a, b) and Upper Wylye (c, d) catchments with error bars representing standard error.

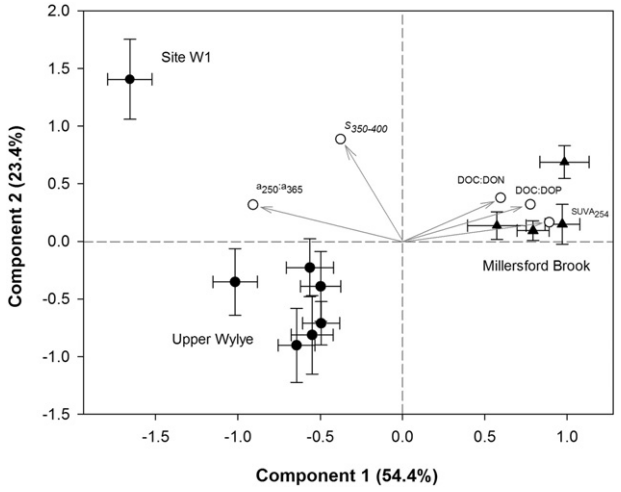

Fig. 6. Correlation bi-plot from PCA on chemical determinands showing cluster centroids grouped by site with standard error.

relationship can be seen in the data, due to the presence of outliers this relationship is not robust and as a result, no single linear regression can explain the relationship between a_{254} and DOC (Fig. 7b). The apparent decoupling between CDOM and DOC in the Upper Wylye further suggests compositionally different material between the catchments as a large number of organic compounds do not absorb UV light at 254 nm. No relationship between elevated flow and these outliers could be identified suggesting the potential mobilisation of flow independent DOM sources.

4. Discussion

4.1. Controls on the delivery of DOM from catchment sources

Over the last two decades there has been a widely documented increase in DOC flux from peat catchments to their waterbodies across both the U.K and areas of mainland Europe (Worrall et al., 2003; Worrall et al., 2004; Evans et al., 2006; Kopáček et al., 2006; Monteith et al., 2007). Due to the multifaceted role DOM plays in the aquatic environment and its role in transferring carbon from terrestrial to aquatic systems such a widespread increase in the flux of reduced carbon is a cause of concern and as a result has focussed research into upland organic rich areas. While some work has been undertaken into lowland areas draining organic-poor soils and groundwater systems, little research exists investigating both compositional differences in DOM and the geological and hydrological controls on the delivery of this material to aquatic systems. In recent years there has been a growing interest in the hydrological function of permeable aquifers and the ways in which this controls stream water chemistry. This has been driven by a lack of understanding of groundwater - surface water interactions combined with the increasing pressures faced by lowland systems from abstraction and agricultural intensification. It is therefore important to develop our understanding of lowland systems to establish if DOM composition remain constant across these environments as the pressures faced by these systems increase, and to determine whether trends identified and conclusions drawn from the extensive research on DOM character and flux in upland systems is applicable and transferable to lowland, intensively farmed and populated catchments. This study attempts to in part tackle this question linking land cover and hydrological processes with instream observations of DOM composition.

It was hypothesised that DOM composition exported from the two study catchments would differ as a function of geoclimatic character and nutrient enrichment status. DOM exported from the lowland peat catchment studied here was found to be similar to that observed across a range of upland peat systems (e.g. Dawson et al., 2009; Austnes et al., 2010) with high DOC, $SUVA_{254}$ and DOC:DON ratios. $SUVA_{254}$ has been linked to a number of bulk molecular DOM measurements including aromatic C content (Weishaar et al., 2003) and carbon normalised yields of lignin (Hernes et al., 2008) with higher $SUVA_{254}$ values reflecting material with a higher bulk aromatic C content and higher carbon normalised yields of lignin. Data collected here suggest the dominance of a terrestrial source in the lowland peat catchment observed during this study. By contrast material exported from the groundwater-dominated agricultural catchment demonstrated lower DOC:DON ratios and $SUVA_{254}$ values suggesting that DOM was compositionally different, with a lower percent bulk aromatic C content. This is logical given the prevalence of mineral soils and the paucity of organic-rich soils in chalk landscapes like the one studied here. In addition this finding fits into research conducted at a global scale into the impact of agriculture on DOM compositional measurements by Graeber et al. (2015) who found agricultural practices to significantly alter DOM composition, observing lower C:N ratios, a higher fluorescence index (Cory and McKnight, 2005) and a lower humification index (Fellman et al., 2010) in catchments with intensive agricultural practices compared to semi natural systems suggesting this material to have a higher reactivity and thus will increase instream productivity and outgassing of CO_2.

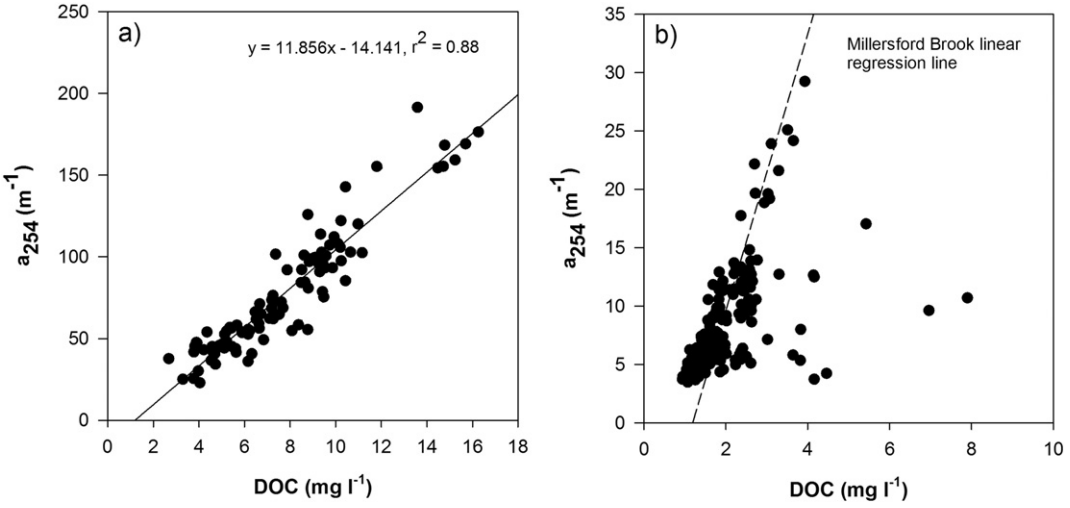

Fig. 7. Relationship between a_{254} and DOC concentrations for (a) Millersford Brook (b) Upper Wylye catchment. Millersford Brook regression line plotted for comparison (dashed line). Note the difference in scale between plots.

However, the Upper Wylye is groundwater dominated, and groundwater DOM is a complex mixture of compounds derived from a wide variety of sources that can include surface water, soil and DOM leached from intensive agricultural production. It is also likely a mixture of ages with groundwater residence times ranging from less than one day to several decades old. As a result it is difficult to infer reactivity based on bulk measurements alone (Weishaar et al., 2003). Work investigating the role of groundwater in controlling the delivery of DOM to systems is sparse. However, groundwater DOM has been found to be altered by microbial processes with recent research reporting the removal of lignin-derived phenols in the unsaturated zone, with the optical properties reported suggesting a higher proportion of lower molecular weight material in groundwater relative to surface waters (Shen et al., 2015). The uptake of polyphenolic compounds by microorganisms in streams has also been previously reported along with the simultaneous removal of higher molecular weight fluorescence components and the production of novel compounds (e.g. Fasching et al., 2014).

Temporal variation in discharge has been noted as a key control on the delivery of DOM fractions to both riverine (Hernes et al., 2008; Spencer et al., 2010) and estuarine systems (Spencer et al., 2007). Seasonality in groundwater recharge observed in this study indicates elevated water table depth during the winter months decreasing during the summer, a pattern common across the groundwater dominated Hampshire Avon (Jarvie et al., 2005). The high connectivity of the Wylye to the underlying aquifer may in part explain the intra-annual variation seen during this study, with groundwater delivering material with a lower aromatic C content relative to surface waters. While this may explain underlying variation across the year studied, heavily impacted small catchment systems such as the Wylye are complex and the DOM chemistry is likely to respond to pulsed delivery of fresh material from catchment sources during high flow events, linked to the mobilisation and flushing of DOM pools from a wide range of source areas, along a diverse set of flow pathways, in addition to flow independent deliveries. Given the significant increase in DOC and DON concentrations observed at site W6 in the Upper Wylye catchment, one such source area is the discharge from Warminster WwTW, with a second significant influx of DOM from the military barracks between sites W6 and W7. Urban land use has been associated with shifts in DOM concentrations and compositions (Aitkenhead-Peterson et al., 2009; Williams et al., 2015). While the potential reactivity of this material and its ecosystem functional role cannot be directly inferred from this study it is worthy of further investigation, as studies have found the proportion of bioavailable DON and DOP in wastewater effluent to be in the region of 73–75% (DOP) and between 28%–61% for DON (Qin et al., 2015). In addition smaller discharges from poorly regulated septic tank systems along the length of this river may pose a significant threat to stream ecosystem health as these too contain elevated concentrations of labile organic and inorganic material and have been found to be widely used and commonly underestimated (May et al., 2011).

While large variations in DOC concentrations were observed in the Millersford Brook catchment across all sampling sites no clear variations in DOM composition were observed across the year studied. Due to the nature of the sampling regime reported here, large variations in flow were captured during sampling of the Upper Wylye, due in part to the predictable nature of its flow regime. Variable flow conditions were captured in Millersford Brook with good hydrograph coverage as seen in Fig. 2 however, no seasonal variation can be observed. This is unsurprising given the flashy nature of the flow regime and its low baseflow index. Variation across both DOC and optical indices is large in Millersford Brook reflecting the pulsed delivery of material during storm events commonly reported in peat dominated catchments (Austnes et al., 2010). In order to fully unravel the complex mosaic of contributing DOM source areas in Millerford brook greater insight could be gained from increased sampling resolution, as has been recently reported across upland catchments (Austnes et al., 2010).

5. Conclusion

Understanding the delivery of organic matter to streams from contributing sources areas in their catchments is a complex problem. Molecular scale determination of DOM composition is difficult to conduct on the high spatial and temporal resolution required to understand the complex connectivity between landscape characteristics instream chemistry. While useful in nutrient source attribution bulk measurements of DOM in the form of DOC, DON and DOP concentrations tell us little about molecular composition of this vast pool of material and therefore its likely ecosystem functional role. Optical measurements adopted in this study indicate that DOM composition varies both temporally and spatially according to landscape character within lowland U.K. catchments over relatively small geographical distance. However, it is the differing hydrological regimes responsible for the connectivity between landscape characteristics and the observed instream chemistry. It is therefore important to fully understand how this composition varies and the drivers behind such variation in order to better understand DOM dynamics in aquatic systems. This is a problem that needs to be addressed across all environments to ensure that conclusions drawn from specific studies on DOM composition in one locale or time period, and the processes and pathways controlling its delivery to and cycling within stream ecosystem are not broadly applied across a range of environments with differing character and function. Results from this study, inferred from the stoichiometric ratios and optical indices applied, suggest significant differences in the composition of DOM exported to lowland rivers from their catchments: while lowland peat catchments demonstrate DOM compositional characteristics similar to upland peat systems, lowland permeable catchments do not share these characteristics. Delivery mechanisms also differ between catchments, controlling intra-annual variation in DOM composition in each catchment. The lack of a statistically robust relationship between CDOM absorbance and DOC concentration in the chalk dominated catchment suggests care is also required when using absorbance measurements as a surrogate for DOC concentrations in systems heavily impacted by human activities, with any relationships derived being heavily catchment specific. DOM exported from permeable catchments has a lower DOC:DON ratio than that previously reported for upland and peatland systems. Taken together with the different optical index values for this catchment, this suggests that DOM exported from this chalk catchment has a lower bulk aromatic C content and lower molecular weight than that exported from peatland systems. As a result this material may differ in its bioavailability, and may play an important role in the ecosystem function and response to nutrient loading in chalk streams.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.06.211.

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